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Solomon Buckman
University of Wollongong, solomon@uow.edu.au

P Ashley
University of New England

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Silica-carbonate (listwanites) related gold mineralisation associated with epithermal alteration of serpentinite bodies

S. Buckman¹ and P.M. Ashley²

¹ School of Earth and Environmental Sciences, University of Wollongong, Australia

² School of Earth Sciences, University of New England, Australia

Keywords: serpentinite, listwanite, silica-carbonate, carbonatization, epithermal, gold

Introduction

The New England Orogen is host to the Great Serpentinite Belt, which occurs along the Peel-Manning Fault System and generally divides rocks of the Tamworth Belt (Gamilaroi terrane) to the west from the accretionary complex rocks of the Djungati terrane (Woolomin Beds) to the east. The serpentinite melange contains exotic blocks of ophiolitic material of Early Cambrian age and HPLT blueschist/eclogite facies metamorphic rocks of Ordovician age (Aitchison and Ireland, 1995). However, there is no evidence of the emplacement of serpentinite melange until the Early Permian as evident by the presence of serpentinite detritus in the Manning Group diamictites. These sediments were deposited contemporaneously with serpentinite emplacement within localised extensional settings associated with strike-slip faulting along the Peel-Manning Fault System (Aitchison et al., 1997). The subsequent intrusion of granite batholiths from the Early Permian to Triassic were the heat engines that drove hydrothermal cells responsible for widespread epithermal mineralisation in the New England Orogen which resulted in the carbonatization of serpentinite protoliths to form silica-carbonate alteration zones or "listwanites". Many of these listwanite bodies contain gold mineralisation in the New England and the telescoped natures of listwanite-related mineralization in other regions suggest that this style of alteration presents a significant exploration target. This paper is a review of the silica-carbonate (listwanite) alteration process and how it relates to serpentinite bodies in the New England Orogen.

The term "listwanite" (alternate spellings - listwaenite, listvaenite or listvanite) was first introduced by Rose (1837) to describe the silica-carbonate alteration of serpentinite in the Urals. Since then the term "listwanite" has remained in use in Eurasia, whilst in America, Canada and Australia, the self-descriptive term "silica-carbonate" has become more prevalent. The terms "listwanite" and "silica-carbonate" are synonymous and encompass all forms of carbonatization from the carbonate-rich to silica-rich phases.

Listwanites are host to world-class gold deposits, such as McLaughlin's Mine in California, but have received little exploration attention in Australia. Listwanites are relatively abundant around the margins of the Great Serpentinite Belt (ophiolitic Weraerai terrane) and may represent a potentially new and rewarding exploration target. The alteration develops along faults that intersect bodies of serpentinized ultramafic rocks and is locally host to sub-economic grades of gold at Nundle, Barraba and Bingara. This paper reviews silica-carbonate alteration processes and the behaviour of gold in listwanites of the New England.

The alteration of serpentinized ultramafic rocks to silica-carbonates is caused by the migration of carbon dioxide-rich fluids along faults, and is sometimes referred to as "carbonatization". Silica-carbonate alteration is commonly observed around the margins of dismembered ophiolite sequences and has been reported by a number of authors worldwide, notably because it is often host to gold, mercury, magnesite and occasionally, base metal mineralisation (Ash and Arksey, 1990a; 1990b; Ashley, 1997; Ashley and Hartshorn, 1988; Auclair et al., 1993; Barnes et al., 1973; Bohlke, 1989; Buisson and Leblanc, 1985; 1986; Efremov, 1952; Knopf, 1906; Madu et al., 1990; Ploshko and Bogdanova, 1963; Pohl, 1990; Sherlock and Logan, 1995; White, 1967).

The formation of silica-carbonate rocks requires a precursor body of serpentinite before this particular style of alteration can evolve. However, the silica-carbonate alteration can migrate into adjacent non-serpentinized/ultramafic rocks. Therefore, it is important to understand a little about the initial serpentinization process. Serpentinization occurs as a result of the hydration of ultramafic rocks, in particular the magnesium silicates such as olivine, pyroxene and amphibole (Klein and Hurlbut, 1985). The reaction can follow different paths depending on the quantity and composition of the fluids and host rock, as shown in equations 1-4. A thorough review of the processes involved in serpentinization has been published by (O'Hanley, 1996).

Serpentinization

The serpentinization process commonly occurs in supra-subduction zones, where wet oceanic crust is being subducted beneath island-arc material. As the oceanic slab descends the pressure and temperature increases resulting in dehydration of the down-going lithologies. The fluids released by dehydration interact with the surrounding ultramafic, mafic and pelagic sediments and the trapped mantle wedge of the overriding plate contains ultramafic rocks that can be readily altered to serpentinite. The serpentinization process is exothermic and can produce temperatures of up to 300°C (Moody, 1976; Wenner, 1972; Wenner and Taylor, 1971; 1973; 1974). The reaction also results in a substantial increase in volume, which can force the ductile serpentinite into faults and fractures where it develops its characteristic schistose fabric. Serpentinite is found extruding out of mud-type volcanoes within present day fore-arc regions, such as the Marianas region (Fryer, 1985, 1992; Fryer and Fryer, 1987; Fryer and Mottl, 1992; Fryer et al., 1999). Serpentinite seamounts or "mud volcanoes" occur 50-120 km from the trench axis in the 200 km wide Mariana forearc. The serpentinite seamounts are interpreted as diapirs and consist of fragments of serpentinite in a serpentine mud composed of serpentine, chlorite, clay and carbonate (Fryer and Mottl, 1992; Lagabriele et al., 1992).

Silica-carbonates (Listwanites)

Listwanites form as a result of the chemical reaction between serpentinite and CO₂-rich fluids. These fluids usually migrate along faults or fractures along the contact of serpentinite and the adjacent country rocks. Freshly broken listwanites have a green-orange colour due to the presence of fuchsite and ferro-magnesium carbonates respectively. The weathered surface of listwanites usually has a gossanous boxwork texture and a brown-red colour due to the preferential breakdown of the ferro-magnesium carbonates (Fig. 1).

Silica-carbonates, as their name suggests are composed of varying proportions of silica - in the form of quartz or chalcedony, and carbonates - in the form of magnesite (with varying proportions of Fe and Ca). Other, less abundant minerals, commonly found in silica-carbonates include chlorite, fuchsite (Cr-rich mica), talc, fluorite, residual serpentine and chromite, and sulfides such as pyrite, chalcopyrite and arsenopyrite.

Studies by Barnes et al (1973) indicate that silica-carbonate rocks from the Coast Ranges, California, are commonly supersaturated with magnesite, dolomite and sometimes siderite and ankerite. All of the samples are undersaturated in brucite, diopside, pyroxene and serpentine (chrysotile) which is the major precursor mineral. The persistence of serpentine in some silica-carbonates is probably an indication that the volume of water required to remove all of the serpentine was not sufficient. The alteration of serpentinite in the presence of silica-rich hydrothermal fluids might be expected to form talc as in reaction 4. However, most silica-carbonates are undersaturated in both talc and tremolite (phases which are richer in silica than serpentine) despite the common occurrence of opaline silica in the silica-carbonates. This is because talc is not a stable mineral at the low temperatures of the springs providing the fluids. Instead the H⁺ produced by the partially dissolved CO₂ gas (reaction 6) is removed by the reaction with serpentine (reaction 8), releasing Mg²⁺ and SiO₄²⁻ into solution.

The chemical reaction involved in the early stages of silica-carbonate alteration can be summarized by reaction 4 (Sherlock and Logan, 1995). Tuysuz and Erler (1993) undertook detailed geochemical studies of silica-carbonates in the Kagizman region, NE-Turkey, and divided the silica-carbonates into two categories, Phase 1 and 2, based on the degree of alteration:

Phase 1 silica-carbonates are much more widespread and partly envelop phase 2 silica-carbonates. Phase 1 silica-carbonates are carbonate-dominated and contain relict serpentinite fragments, while phase 2 silica-carbonates are rich in silica and often host to economic grades of gold. These two contrasting assemblages (Phase 1 and 2) have been noted by many authors describing silica-carbonates but with varying terminology.

Phase 1 silica-carbonates are also referred to as “talc-carbonate schists”, while phase 2 silica-carbonates have been termed “birbirite” (Auclair et al., 1993).

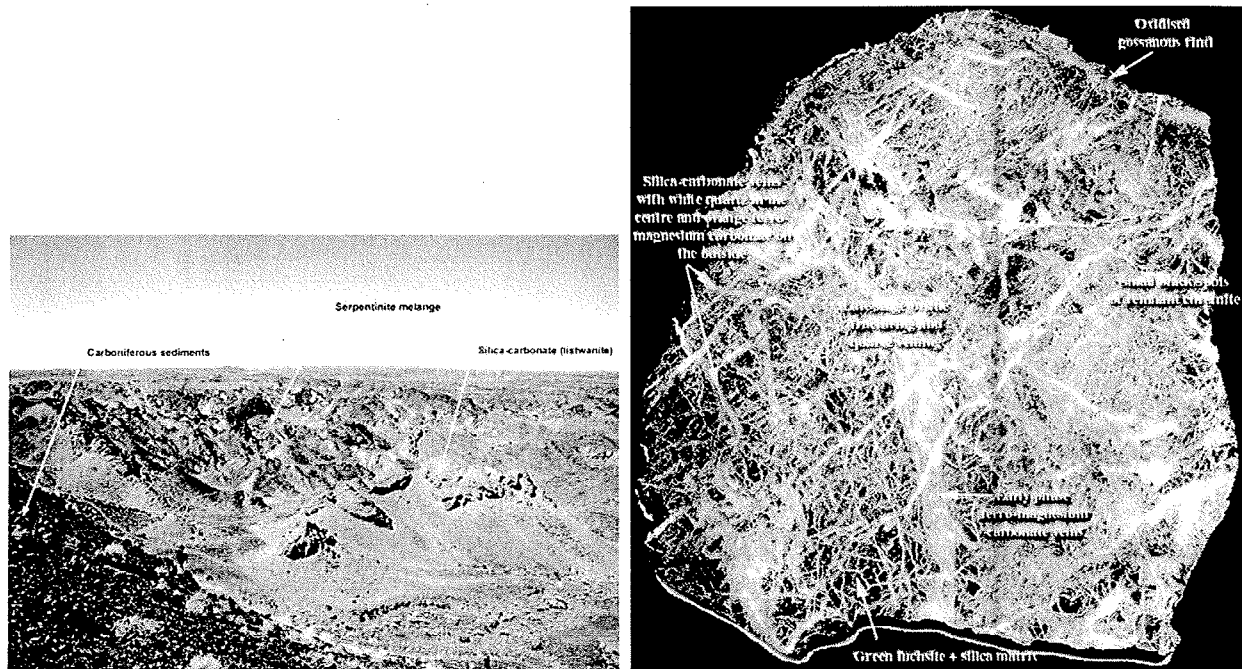


Fig. 1 A) The distinct orange listwanite alteration in outcrop formed on the margins of the Sartuohai ophiolitic melange in NW China and host to significant gold mineralisation locally (Buckman, 2000). B) Listwanite slab from Sartuohai showing early stage carbonate veining and a green fuchsite + silica matrix and late stage quartz/chalcedony veins in white (width of slab is 20 cm).

Phase 1 silica-carbonates

Phase 1 silica-carbonates are composed of varying proportions of carbonates, principally dolomite, ankerite, magnesite, and rarely siderite, calcite, magnesite and serpentinite. According to Tuysuz and Erler (1993), generation of Phase 1 silica-carbonates begins where the value of MgO decreases to about 32% and they persist to MgO content of 15% while the silica concentrations can drop to as low as 5%. They calculated that the transition from serpentinite to Phase 1 listwanites involves an overall volume increase of 63% based on the assumption is immobile during the alteration process. This equates to a loss in MgO (~28%) and SiO₂ (~36%). In contrast, there is an overall increase in the concentration of CaO (96%) and CO₂ (95%) in the form of carbonate minerals. The mean trace element contents indicate phase 1 silica-carbonates are enriched relative to serpentinite in Ni (13%), Co (27%), Cu (78%), and As (87%), while Au decreases by about 29% from serpentinites to phase 1 silica-carbonates.

The decrease in gold concentration highlights an important process because it identifies the Phase 1 listwanites as the alteration stage at which gold is freed from serpentinite and dissolved into solution. For economic gold deposits to form it is vital that this process of gold scavenging occur through a large volume of source rocks and that the gold-rich fluids are channelled into a relatively small zone in which pressure, temperature and chemical conditions favour the precipitation of gold from solution. Such conditions usually occur closer to the surface as a result of the interaction with meteoric water and decreases in temperature and pressure. These conditions also give rise to the formation of Phase 2 silica-carbonates.

Phase 2 silica-carbonates

Phase 2 silica-carbonates consist predominantly of silica in the form of quartz, chalcedony and rarely opal. Carbonate minerals are either minor constituents or totally absent. Phase 2 silica-carbonates are characterised by the introduction of silica. The same two assumptions as above apply (Tuysuz and Erler, 1993), and based on a volume increase, MgO loss is 36% from phase 1 to phase 2 silica-carbonates and CaO loss is about 21%. There is a major increase in Au (52%), in the transition from phase 1 to phase 2 silica-carbonates with very little increase in Cu (7%) and As (3%).

Assuming a constant volume, phase 2 silica-carbonates show a loss in MgO (78%) and CaO (35%), but gains in SiO₂ (30%), CO₂ (94%), and K₂O (98%). In the trace elements, there are gains in Au (21%), Cu (76%) and As (84%). Co and Ni contents of phase 2 silica-carbonates relative to serpentinite decrease by 48% and 66% respectively (Tuysuz and Erler, 1993).

Chemical reactions involved in the serpentinization process (1-3) (O'Hanley, 1996) and the carbonatisation (listwanite) process (5-10).

	olivine	water		serpentinite	brucite
1)	2Mg ₂ SiO ₄	+ 3H ₂ O	→	Mg ₃ Si ₂ O ₅ (OH) ₄	+ Mg(OH) ₂
2)	3Mg ₂ SiO ₄	+ 4H ₂ O + SiO ₂	→	2Mg ₃ Si ₂ O ₅ (OH) ₄	
	olivine	orthopyroxene		serpentinite	
3)	3Mg ₂ SiO ₄	+ MgSiO ₃ + H ₂ O	→	Mg ₃ Si ₂ O ₅ (OH) ₄	
	Serpentine	+ silica	→	talc	+ water
4)	Mg ₃ Si ₂ O ₅ (OH) ₄	+ 2SiO ₂	→	Mg ₃ Si ₄ O ₁₀ (OH) ₂	+ H ₂ O
5)	Serpentinite + carbonic acid + silicic acid → magnesite + water + silica				
	Mg ₃ Si ₂ O ₅ (OH) ₄ + 3H ₂ CO _{3(aq)} + (n)H ₄ SiO _{4(aq)} → 3MgCO ₃ + (5+2n)H ₂ O + (2+n)SiO ₂				
	Carbon dioxide + water → carbonic acid				
6)	CO ₂	+ H ₂ O	→	H ⁺ + HCO ₃ ⁻	
7)	HCO ₃ ⁻	→	H ⁺ + CO ₃ ²⁻		
8)	6H ⁺ + Mg ₃ Si ₂ O ₅ (OH) ₄	→	3Mg ²⁺ + 2H ₄ SiO ₄ + H ₂ O		
	MgFe-carbonate + silicic acid → silica + carbon dioxide + water + Mg, Fe ions				
9)	MgFe(CO ₃) ₂	+ 4H ⁺ + SiO ₄ ⁴⁻	→	SiO ₂ + 2CO ₂ + 4H ₂ O + Mg ²⁺ + Fe ²⁺	
10)	nMg ²⁺ + mFe ²⁺ + 4HCO ₃ ⁻	→	{n/(n+m)}Mg{m/(n+m)}Fe(CO ₃) ₂	+ 2H ₂ O + 2CO ₂	

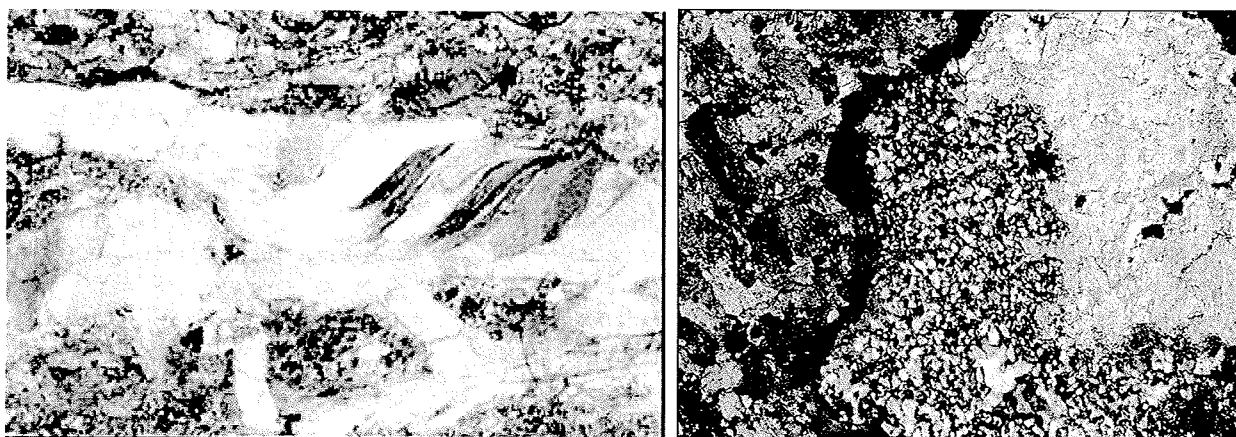


Fig. 2 A) A carbonate-rich listwanite from the Sartuohai 1 Gold Mine. The carbonates have pseudomorphed the original S-C fabric (dextral) of the schistose serpentinite. Small (grey-blue) patches of amorphous silica have started to develop and overprint the carbonates. B) A silica-rich listwanite (phase 2) in which chalcedony is replacing the earlier formed carbonates. This marks the transition from alkaline to acidic conditions and often corresponds with gold mineralisation.

According to Barnes et al., (1973), if CO_2 is present in the system as a gas, it controls the pH maintaining acidic conditions. Serpentine will react to yield Mg^{2+} , Fe^{2+} and SiO_4^{4-} in solution (reaction 8). The silica released into solution as silicic-acid precipitates as amorphous silica at lower temperatures, which in time forms β -cristobalite. Based on chemical potentials, magnesite, dolomite, and siderite or ankerite may be expected to precipitate from solution because the H^+ is being consumed in the reaction with serpentine (reaction 8) leaving the excess HCO_3^- to react with the Mg^{2+} and Fe^{2+} ions (reaction 10) to precipitate ferroan magnesite. The production of excess water and carbon dioxide in reaction 10 provides positive feedback to the carbonic acid reaction in reaction 6, thus accelerating and sustaining the process. Calcite only precipitates rarely because saturation with calcite is less common than saturation with magnesite or dolomite.

The above reactions form part of an open system, in which, two processes are competing, the consumption of H^+ by the reaction with serpentine (reaction 8), and the supply of H^+ by solution of CO_2 (reaction 6) (Barnes et al., 1973). However, if the serpentine reservoirs adjacent to the channels of fluid flow become exhausted before CO_2 is diminished, the pH of the fluid will remain low due to the high PCO_2 , and because the H^+ is no longer being consumed in the breakdown of serpentine. There will no longer be a steady supply of Mg^{2+} because the breakdown of serpentine is no longer occurring, which means the precipitation of carbonate minerals will also cease. This is point at which the Phase 1 listwanites begin the transformation to silica-rich, Phase 2 listwanites. The fluids become increasingly acidic, due to the high PCO_2 and they are rich in dissolved silica from the initial breakdown of serpentine (reaction 8). These acidic fluids begin to dissolve the existing carbonate assemblage and replace them with almost pure silica. In the process more CO_2 is released (reaction 9) thereby further driving the carbonic acid reaction (reaction 6) and increasing the acidity of the fluids. The Mg^{2+} and Fe^{2+} released into solution by the breakdown of the carbonates are probably channelled along the fault and precipitated as carbonates in more suitable conditions (higher pH and temperature). This may explain why small listwanite zones can be found along faults that extend into surrounding country rock with no initial serpentine protolith.

In contrast to reaction 9, the CO_2 flux in the system may be insufficient to maintain free CO_2 gas throughout the flow path due to; 1) a low CO_2 flow from the source, 2) a long reaction path (serpentine only), or 3) the presence of brucite, pyroxene or olivine (Barnes et al., 1973). The presence of serpentine alone yields pH values of more than 8 (Barnes and O'Neil, 1969). Brucite yields even higher pHs and pyroxenes and olivine yield the highest pHs of all. As the pH increases, so does the CO_3^{2-} activity (reaction 7). The result is the abundant deposition of carbonate minerals (chiefly magnesite because Mg^{2+} is much more abundant in serpentine than Ca^{2+} or Fe^{2+}). If the high PCO_2 fluids react with pyroxene or olivine, the pH values may exceed 11 and the silica yielded by hydrolysis will be largely ionised as SiO_4^{2-} . Mg^{2+} will be immobile with very high CO_3^{2-} activities and magnesite would be expected to form with very little or no silica. This process probably explains the origin of many silica-carbonate hosted magnesite deposits (Barnes et al., 1973).

The silica-carbonate alteration process is largely dependent on the outcome of intermediate reactions and the rate at which they occur. Of most importance is the total concentration of carbon dioxide within the system as this affects the pH of the circulating fluids. High pH favours the precipitation of carbonates while low pH favours the precipitation of silica (Barnes et al., 1973). Carbonate minerals form under high temperatures ($>100^\circ\text{C}$) and high pH (>8) but they can be easily redissolved by low-temperature and weakly acidic solutions. The opposite is true for silica, as it is more readily ionised in hot basic solutions but precipitates as amorphous silica or quartz veins at low temperatures and pH. Most hydrothermal or metamorphic events naturally progress from hot to cold as the heat source diminishes. Thus the precipitation of silica usually marks the final stages of silica-carbonate alteration and cross-cuts all previous mineral assemblages (Fig. 1). The stability of silica, once precipitated, is high enough that it can be regarded as an irreversible reaction at the relatively low temperatures associated with silica-carbonate alteration. The carbonates on the other hand can be readily dissolved and re-precipitated so there may be several generations of carbonates within a single listwanite. This is the reason why most listwanites evolve along a linear path of silica enrichment and carbonate diminishment, after the initial formation of the Phase 1 listwanites. This process often results in the formation of a silica core surrounded by the intermediate ferromagnesium carbonates.

The hydrothermal system involved in silica-carbonate alteration is open to two components, water and carbon dioxide. Based on isotopic data (δO^{18} and δC^{13}), Barnes et al., (1973) favour the interpretation of locally derived meteoric waters mixing with metamorphic derived CO_2 . The extent of the alteration depends on the influx of gas and water from their respective sources. Stable isotope data also indicate that temperature plays a significant role in determining the composition of the listwanite. The isotopic compositions of silica-rich cores of listwanites (Auclair et al., 1993; Sherlock et al., 1993) show that they

formed at low temperatures while the surrounding carbonate assemblage formed at much higher temperatures.

Gold in listwanites

Based on geochemical studies of silica-carbonates from ophiolite complexes in Liguria, Morocco and Saudi Arabia, (Buisson and Leblanc, 1987) concluded that silica-carbonates are similar in style to Archean carbonatized ultramafic rocks with economic grades of gold being reached in sulfide-rich zones and late quartz veins. Ultramafic rocks (upper mantle peridotites) are believed to be the main source of gold (Pipino, 1980), which is contained within the accessory opaque minerals (sulfides, chromite, and magnetite). Gold contents in serpentinized mantle peridotite range between 3 and 5 ppb. Large-scale hydrothermal systems operating during the late stages of tectonic emplacement leach gold from the opaque minerals and transport it in a CO_2 -S-As-Cl-Na-K-B-rich solution as thio-arsenic complexes. The hydrothermal fluids are focussed along tectonic contacts. As the system evolves the acid gold-bearing solutions precipitate silica-pyrite-arsenides and gold when entering into the reducing and alkaline carbonatized rocks.

Silica-carbonates are on average 5 – 20 times more enriched in gold (average 0.02 – 0.1 ppm Au) than the surrounding ultramafic rocks (between 0.001-0.010 ppm) (Buisson and Leblanc, 1987). Economic grades of gold are usually associated with sulfides, sulfarsenides or arsenides (Buisson and Leblanc, 1985; 1986; 1987; Leblanc, 1986; Leblanc and Billaud, 1982). The gold is usually bound to the sulfides, with pyrite grading between 10 and 50 ppm, and Co-arsenides between 10 and 100 ppm. Small gold grains are observed around limonitized pyrite grains as a result of weathering and oxidation. Trace element analyses show strong positive correlations between Au and As, and quite commonly K. Elements such as Ba, Sb, B, Bi, Ag, and Cu may also be associated with high gold values.

Buisson and Leblanc (1987) concluded that during the serpentinization process half the gold is concentrated into magnetite and secondary sulfides. These opaque minerals are subsequently destroyed in talc-carbonate alteration zones (Phase 1 listwanites), which results in gold being released from the serpentinite wall rocks and transported in solution. The gold- and silica-rich fluids are transported to higher crustal levels where the change in conditions (lower temperature, pH and $f(\text{O}_2)$) results in the precipitation of gold, quartz and sulfides.

Mercury in listwanites

Silica-carbonate mercury deposits have been widely reported from the California region and account for 85% of mercury production in the United States (Davis, 1966; Sherlock and Logan, 1995). These mercury deposits generally have low gold concentrations (< 5 ppb) however, there have been rare occurrences of elevated gold concentrations (Vredenburg, 1981), most notably in zones associated with petroliferous chalcidonic veins (Peabody and Einaudi, 1992; Sherlock and Logan, 1995). Three styles of mercury deposit occur in northern California: (1) Those associated with the Geysers Geothermal System, such as the Culver Baer deposit (Peabody and Einaudi, 1992), composed of magnesite-chalcidony-cinnabar veins hosted within silica-carbonate altered serpentinite. (2) Fractured silica-carbonate containing veins of cinnabar and no other gangue minerals, and; (3) a less common style of deposit containing disseminated cinnabar in limonitic altered greywacke.

Platinum in listwanites

Fischer et al., (1987) touched on the prospect of PGE mineralisation associated with serpentinites and carbonatized ophiolitic rocks at Bou-Azzer, Central Anti-Atlas. Platinum, palladium and gold are believed to be concentrated as Ni-Fe sulfides or arsenides along with chromite in small residual basaltic magma chambers. The process of serpentinization destroys the ultramafic mineral assemblage resulting in the formation of lizardite, chrysotile and magnetite. The process induces a decrease in oxygen fugacity and allowing PGE's and gold to be concentrated in magnetite. The serpentinization process does not seem to affect the overall PGE concentration (Oshin and Crockett, 1982) so the magnetite PGE patterns are representative of PGE distribution in the primary surrounding host-rocks. Gold is often found in much lower concentrations in magnetite compared to the PGE's. During subsequent silica-carbonate alteration of serpentinite the oxides and sulfides are destroyed by acidic hydrothermal solutions (Buisson and Leblanc, 1987) and PGE's and gold are transported in solution as Cl, S or As complexes (Bischoff and Seyfried, 1978). Gold will precipitate from this solution at low temperatures in a reducing environment but the behaviour of PGE's in this process is not well understood. As PGE concentrations in magnetite of the

original serpentinite are greater than gold, it would be expected that PGE concentrations would also be high in the sulfides and arsenides found in most listwanite gold deposits. However, analytical data show that PGE contents are generally low and do not correlate with gold. It appears that the PGE were less mobile than Au during this type of hydrothermal alteration. This is accounted for, as the solubility of Pt and Pd as Cl-complexes is low between temperatures of 25°C and 300°C. In addition, platinum readily forms arsenides and gold does not, indicating that the amount of platinum that can be transported in As-rich fluids is very low compared to gold. PGE's probably occur as discrete pockets of mineralization, such as sperrylite (PtAs_2) as described by (Hudson and Donaldson, 1984) at Kambalda. There, the PGE mineralization is interpreted as a product of low temperature hydrothermal activity (300°C). As yet there is no satisfactory explanation as to what happens to the PGE's when magnetite is destroyed in the carbonatization process. Maybe platinum is precipitated at much deeper levels within a fault-system where temperatures are much higher (300°C+).

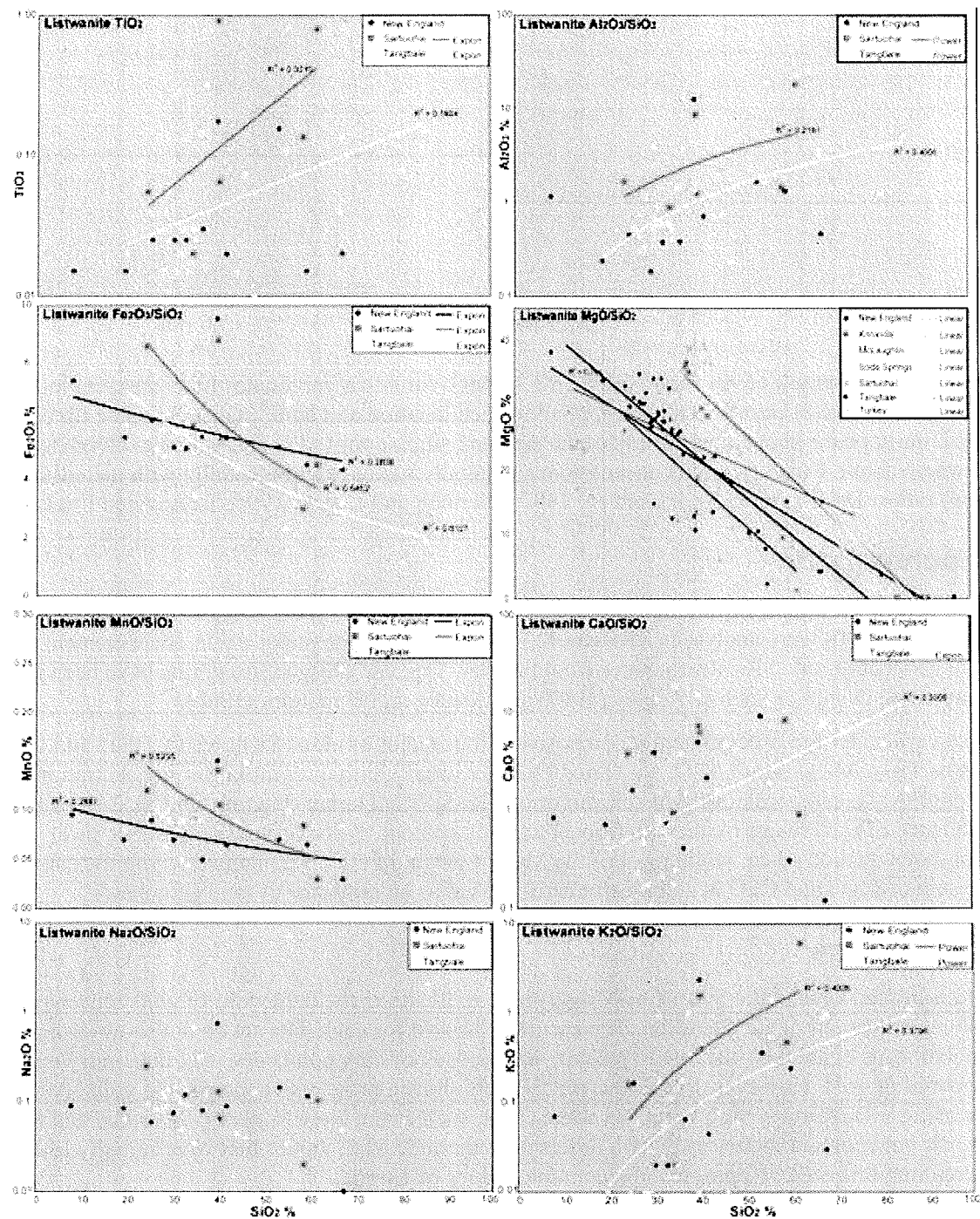


Fig. 3 Plots of the major elements vs. silica content for listwanite rocks of Tangbale, Sartuohai and the New England Orogen. In the case of MgO extra data has been added from analyses taken from Northern California - McLaughlin, Knoxville, Soda Springs (Sherlock and Logan, 1995), and from Turkey (Tuysuz and Erler, 1993).

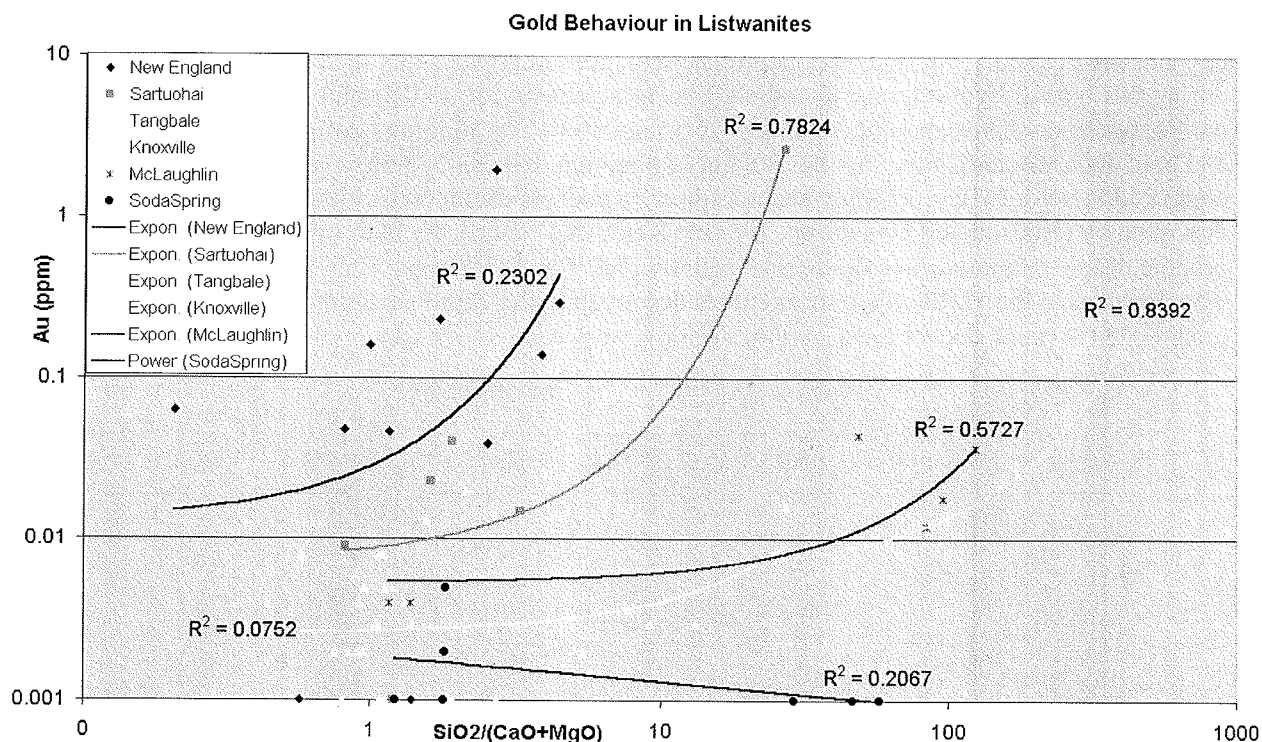


Fig. 4 A scatter-graph of Au versus $\text{SiO}_2/(\text{CaO} + \text{MgO})$ for silica-carbonates from different locations. An exponential curve of best fit has been applied to each location and an R^2 statistical value for each curve is stated. Early phase listwanites are carbonate-rich and silica-poor (<1), while more evolved listwanites plot anywhere above 1 (right). Gold concentrations generally increase exponentially with increasing $\text{SiO}_2/(\text{CaO} + \text{MgO})$ ratios. Data sourced from (Ashley, 1997; Sherlock and Logan, 1995; Tuysuz and Erler, 1993).

Geochemistry

Silica-carbonate samples from the New England and NW China (West Junggar - Tangbale and Sartuohai) (Buckman, 2000) were analysed (XRF and ICP-MS) to determine major oxide, trace element, and precious metal concentrations. Silica-carbonates from the New England Orogen, Australia, have been well documented in studies such as Ashley (1997) and Ashley and Hartshorn (1988).

Silica-carbonates are predominantly composed of four major oxides - SiO_2 , MgO , FeO^* and CaO . Oxides such as TiO_2 , Al_2O_3 , MnO , K_2O , Na_2O and P_2O_5 are usually only present in low concentrations ($<1\%$), although Al_2O_3 can occasionally reach values of $\sim 18\%$. The Harker diagrams in Fig. 3 show the relative abundance of each major oxide with respect to silica content. Silica occurs as quartz veins or amorphous/opaline silica, while most of the MgO , CaO and FeO^* is contained within the carbonate minerals. The sum of MgO and CaO in silica-carbonates is used as an indicator of total carbonates.

Conclusions

Gold is plotted against the $\text{SiO}_2/(\text{CaO} + \text{MgO})$ ratio to illustrate the behaviour of gold concentrations with evolving silica-carbonate alteration. The curves of best fit for each data set do not show strong statistical correlation, as evident by the low R^2 values, and the lack of data points does not help in trying to model the behaviour of gold. However, five of the six data sets show a progressive increase in gold content with an increasing $\text{SiO}_2/(\text{CaO} + \text{MgO})$ ratio. In some cases, such as the New England, Sartuohai and Knoxville data sets, the gold content increases by two orders of magnitude from values that were initially little more than background levels (0.01 ppm) to sub-economic values of 1 ppm.

The exponential increase in gold, illustrated in Fig. 4 has important ramifications for gold exploration in ophiolitic terranes. Given that the initial $\text{SiO}_2/(\text{CaO} + \text{MgO})$ ratio for serpentinite is ~ 0.8 , there appears to be only minor differences in gold concentrations of serpentinites from different regions (0.001 - 0.01 ppm). Gold deposits are not known to occur purely within unaltered serpentinite bodies, which rules out the serpentinitization process as a gold mineralizing process. However, gold concentrations appear to increase

dramatically as the silica-carbonate alteration process creates listwanites with a $\text{SiO}_2/(\text{CaO} + \text{MgO})$ ratio

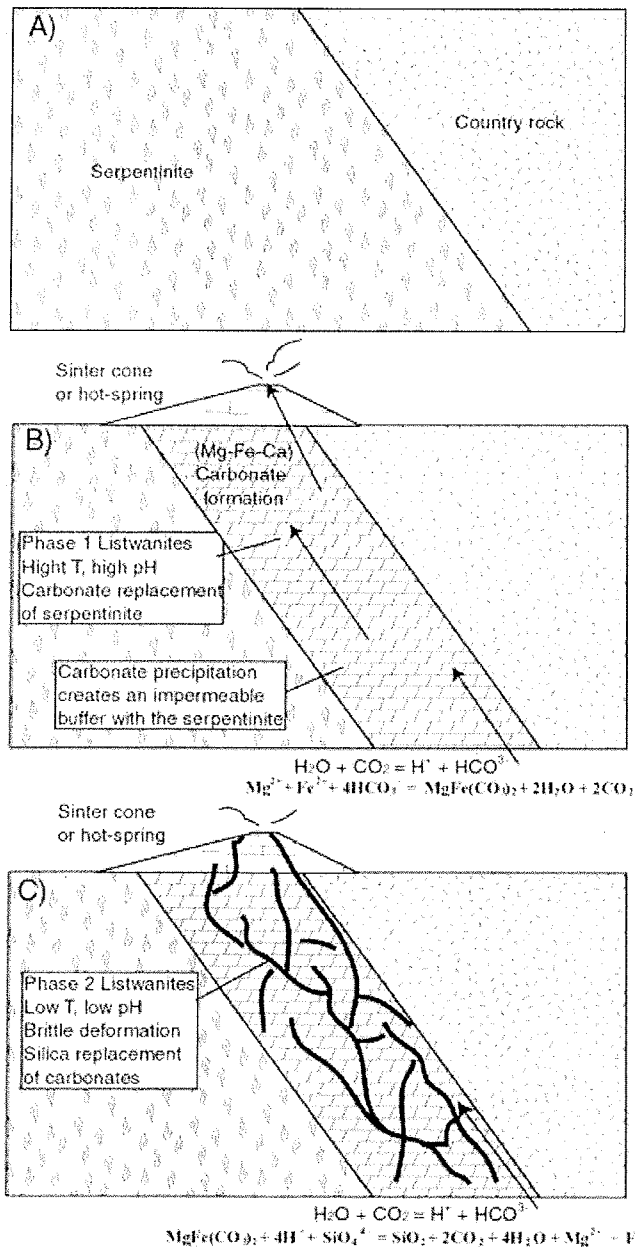


Fig. 5 Idealised petrogenetic model of silica-carbonate alteration based on field observations, petrography and geochemistry. A) Original serpentinite protolith. B) Carbonate-rich listwanites develop as CO_2 -rich hydrothermal fluids permeate through the serpentinite breaking it down and precipitating Mg-Fe-Ca carbonates in its place. Gold is released into solution as a sulfide complex at this stage. C) Silica-rich listwanites form because the hydrothermal fluids are buffered from the serpentinite by the precipitation of carbonates in the first phase of alteration. Consequently, fluids become progressively more acidic favouring the dissolution of carbonates and the precipitation of silica, sulfides and gold.

There are other variables that affect gold mineralization, such as the composition of the wallrock (Bohlke, 1989), pressure and temperature (Sherlock and Logan, 1995) and the composition of the fluids (Cameron, 1989). However, the main source of gold in listwanites is thought to be derived from the chemical breakdown of serpentinite and the dissolution of gold-rich oxides such as magnetite (Buisson and Leblanc, 1987). Thus if the initial gold content in the serpentinite is high (>8 ppb) then the potential for forming economic gold deposits is much higher than for serpentinites that contain only 5 ppb less gold. Extensive periods of silica-carbonate alteration tend to produce silica-rich listwanites, which commonly contain higher concentrations of gold.

greater than 1. Highly evolved listwanites regularly contain economic grades of gold (>1 ppm). It appears from the graph in Fig. 4 that small variations in initial gold content can have dramatic effects on the final gold concentrations in highly evolved listwanites. Gold appears to display non-linear behaviour in listwanite evolution by being extremely sensitive to initial concentrations. If there is very little (<0.002 ppm) or no gold in the initial serpentinite then gold concentrations will rise much above 0.01 ppm even in highly evolved silica-carbonates. However, given an initial gold concentration of around 0.01 ppm in the serpentinite, as with the trend lines for Satuohai or New England (Fig. 4), the process of silica-carbonate alteration can increase gold concentrations to over 1 ppm for $\text{SiO}_2/(\text{CaO} + \text{MgO})$ ratios of only 2. Lower initial serpentinite values of 0.005 ppm may require $\text{SiO}_2/(\text{CaO} + \text{MgO})$ ratios of between 10-100 before economic grades of gold are attained.

An important aspect of this study is that gold mineralization in silica-carbonate rocks appears to be highly dependent upon two variables. The first is the initial gold concentration of the serpentinite protolith. An initial difference of only 10 ppb Au in the serpentinite may result in a difference of 100's or 1000's ppb gold after the process of silica-carbonate alteration has produced silica-rich listwanites. The second variable is the duration of silica-carbonate alteration. Longer or multiple phases of alteration lead to the development of silica-rich listwanites and gold concentrations tend to increase exponentially with increasing silica content.

Gold mineralization in silica-carbonates is highly dependent upon the initial gold concentrations in the serpentinite protolith and the duration of silica-carbonate alteration. Gold is believed to be scavenged from magnetite in the serpentinite (Buisson and Leblanc, 1985; 1987), which is dissolved by the initially basic, hot fluids. Gold remains in solution as a sulfide complex (AuH_2S) and can be transported large distances along conduits such as fault planes. Gold is precipitated from solution only when the pH, temperature and/or pressure drop to the appropriate levels. This may occur as a result of the interaction of the auriferous fluids with slightly acidic, cool meteoric water close to the surface, or the fluids may encounter an anomalous rock type which favours localised precipitation of gold and sulfides (Bohlke, 1989). Alternatively, the chemistry of the entire metasomatic system may change if the serpentinite is entirely spent in the reaction or completely buffered from the fluids, resulting in widespread disseminated gold and sulfide mineralization.

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